

Original Research

Capacitance, charge dynamics, and electrolyte-surface interactions in functionalized carbide-derived carbon electrodes

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Abstract

This study analyzed the dynamics of ionic liquid electrolyte inside of defunctionalized, hydrogenated, and aminated pores of carbide-derived carbon supercapacitor electrodes. The approach tailors surface functionalities and tunes nanoporous structures to decouple the influence of pore wall composition on capacitance, ionic resistance, and long-term cyclability. Quasi-elastic neutron scattering probes the self-diffusion properties and electrode-ion interactions of electrolyte molecules confined in functionalized pores. Room-temperature ionic liquid interactions in confined pores are strongest when the hydrogen-containing groups are present on the surface. This property translates into higher capacitance and greater ion transport through pores during electrochemical cycling. Unlike hydrogenated pores, aminated pores do not favorably interact with ionic liquid ions and, subsequently, are outperformed by defunctionalized surfaces.

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1. Introduction

A growing number of grid-storage, automotive, and portable electronics devices are relying on electrochemical capacitors to efficiently store and output electrical energy [1,2]. These energy storage systems, which are commonly known as supercapacitors, employ electrosorption of ions from electrolytes into carbon electrodes to assemble a double layer of charge on highly porous surfaces [3]. This approach relies on the high specific surface areas of electrode structures ($500\text{--}2500\text{ m}^2\text{ g}^{-1}$) and rapid ion dynamics ($< 1\text{ s}$) to maximize, respectively, the energy and power densities of such systems [4,5]. In addition to maximizing the capacitance, operating voltage window, and long-term cycle lives of these systems, many research efforts are

currently investigating the fundamental charge storage mechanism and decoupling key parameters that govern electrode–electrolyte interactions and dynamics. This crucial knowledge is required for future material and device design of high-performance supercapacitors.

Most prior work has investigated strictly the influence of pore size in carbon electrodes (typically in the 0.5–2.0 nm diameter range) [6] and the influence of the ion to pore-size ratio on capacitance [7]. These computation and experimental efforts mostly implemented a coarse-grained approach and assumed the pores and ions as, respectively, defect-free surfaces and hard spheres [8]. However, emerging research has also highlighted substantial differences between bulk (outside of particles) and confined electrolyte (inside of pores) [9]. In addition to pore size, surface functional groups (oxygen, nitrogen, halogen, etc.) significantly influence ion dynamics and densities in pores *via* intermolecular interactions and steric repulsions [10]. These electrostatically-driven effects are unique for specific ions and solvents, since each electrode–electrolyte combination features different dipole moments and

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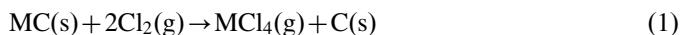
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molecular dimensions [11]. Although multiple existing studies have attempted to decouple these factors, they (1) mostly rely on MD simulations without experimental data support, (2) typically assume a planar graphene or external surface of a nanotube with no ion confinement, and (3) cannot fully correlate electrostatic interactions at the fluid–surface interface with specific capacitance values and rate handling abilities [7,12,13]. There is considerable practical interest in investigating these properties: H- and N-rich groups may improve electrochemical stability, enhance ion density in narrow pores, and add pseudocapacitive contributions.

Carbide-derived carbons (CDCs) exhibit high specific surface areas ($1000\text{--}2500\text{ m}^2\text{ g}^{-1}$) and exceptionally well-defined subnanometer ($d_{\text{av}} \approx 0.5\text{--}1.2\text{ nm}$) porosities [14]. Subsequently, as supercapacitor electrodes, they yield high gravimetric capacitance (above 150 F g^{-1} in organic electrolyte) and find use in both fundamental electrosorption studies and in commercial applications [15]. They are typically synthesized at $200\text{--}1200\text{ }^\circ\text{C}$ using the following reaction (M being an element such as Ti or Si) [16]:



These materials are typically annealed with H_2 (g) or NH_3 (g) at $600\text{ }^\circ\text{C}$ after synthesis to remove any residual Cl_2 [17]. Since the newly synthesized carbon structure has a chemically unstable surface (dangling bonds, lone pairs, and chemisorbed chlorides), these annealing steps selectively deposit functional groups and graft treatment-specific chemical species onto pore walls [18]. Typically, hydrogenation yields the C–H functional groups, while amination yields a heterogeneous mixture of C–N groups (C=NH, C–NH₂, quaternary nitrogen, etc.). Our previous approach stripped chemical groups from surfaces and increased graphitization in amorphous CDCs via $700\text{--}1800\text{ }^\circ\text{C}$, 10^{-6} Torr vacuum annealing [19]. These findings showed that defunctionalized, defect-free CDC surfaces exhibited lower capacitance but improved ion dynamics compared to unannealed CDCs with initial robust, heterogeneous surface chemistry compositions [20]. Although virtually every CDC electrode material tested in supercapacitor configurations has included one of these surface chemistry makeups (with hydrogen being most common), very few studies have addressed the influence of these functional groups on electrochemical performance. Most efforts have focused on extracting pseudocapacitive contributions to total charge densities by encouraging pH and surface charge-dependent interactions between pore wall chemical species and redox-active proton transfer electrolytes [21], such as aqueous KOH and H_2SO_4 . [22] However, novel room-temperature ionic liquid (RTIL) electrolytes do not engage in such H^+ transfer reactions [23,24]. Surface groups primarily influence RTIL interactions with pore walls via Coulombic coupling, steric interactions, and variations in pore filling densities [10]. Furthermore, conventional spectroscopy and elemental analysis techniques often struggle to properly quantify hydrogen (which is inaccessible to spectroscopy) and other functional groups on porous, semi-amorphous carbon such as activated carbon [18]. To improve the accuracy of computational analyses and properly tie them with experimental systems,

research efforts must combine electrochemical analysis of supercapacitor devices with comprehensive characterization of confined electrolytes and their fundamental dynamics inside of pores.

Our work compares the influence of three well-defined surface chemistries on pore walls of CDCs: defunctionalized (annealed), hydrogenated, and aminated. This approach focuses on electrodes with nearly-identical pore size distributions to properly decouple the influence of ion confinement from electrode surface composition. Electrochemical testing and intrinsic characterization evaluates interactions of divergently functionalized pores with a common ionic liquid electrolyte, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{EMIm}^+][\text{TFSI}^-]$). To compare the surface compositions and investigate resulting changes on ion dynamics, we rely on quasi-elastic neutron scattering (QENS) measurements using a high energy-resolution backscattering neutron spectrometer [25]. This approach measures diffusion of mobile species by analyzing broadening of the scattering signal in the range of energy transfers from $\pm 3.4\text{ }\mu\text{eV}$ (the resolution limit of the spectrometer) to $\pm 100\text{ }\mu\text{eV}$ [26]. QENS relies on the large incoherent neutron scattering cross-section of hydrogens compared to other elements to investigate self-diffusion and relative mobility properties of confined electrolyte ions. This measurement technique compares the molecules' respective relaxation times and fraction of elastic scattering in the total scattering signal [27]. Since all hydrogens in $[\text{EMIm}^+][\text{TFSI}^-]$ are attached to the imidazolium ring and alkyl chains, scattering from cations dominates the measured signal. Neutron-measured ion mobility correlates with their behavior under applied potentials in supercapacitor electrodes and shows the significant influences that H- and N-containing surface groups have as compared to defect-free pore walls. In addition to investigating capacitance and ion dynamics, we examine the influence of surface chemistry on ionic resistance and how that, in turn, affects long-term cyclability of these devices. Beyond CDC, these results are applicable to other carbon electrodes, such as activated carbon and graphene, which can be selectively functionalized using furnace and wet chemistry treatments.

2. Methods

2.1. Material synthesis

We synthesized carbide-derived carbons according to a previously developed procedure. [28] Titanium carbide (TiC) particles ($1\text{--}5\text{ }\mu\text{m}$, 99% pure, Alfa Aesar) were loaded into a quartz boat and placed in a quartz tube furnace. After flowing Ar gas purged the environment 1 h, the furnace ramped up to $800\text{ }^\circ\text{C}$, and the material was subjected to pure flowing Cl_2 gas for 6 h in the isothermal condition. The furnace then cooled down to $600\text{ }^\circ\text{C}$ in Ar gas, H_2 gas annealed the material for 3 h, and, finally, the furnace cooled down to room temperature. This material is hereafter referred to as “Initial CDC.”

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